

Hydrogen for oil refining via biomass indirect steam gasification: energy and environmental targets

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Abstract The energy and CO₂ consequences of substitution of a fossil-fuel-based hydrogen production unit with a biomass-based process in a large European refinery are studied in this study. In the base case, the biomass-based process consists in atmospheric, steam-blown indirect gasification of air-dried woody biomass followed by necessary upgrading steps. The effect of gradually substituting the current refinery hydrogen production unit with this process on global energy and CO₂ targets is estimated first. Few process concepts are studied in further detail by looking at different degrees of heat integration with the remaining refinery units and possible polygeneration opportunities. The proposed process concepts are compared in terms of energy and exergy performances and potential reduction in refinery CO₂ emission also taking into account the effect of marginal electricity. Compared to the base case, an increase by up to 8 % points in energy efficiency and 9 % points in exergy efficiency can be obtained by exploiting process integration opportunities. According to energy efficiency, steam production appears the best way to use excess heat available in the process while electricity generation through a heat recovery steam cycle appears the best option according to exergy efficiency results. All investigated cases yield to significant reduction in CO₂ emissions at the refinery. It appears in particular that maximal emission reduction is obtained by

producing extra steam to cover the demand of other refinery units if high efficiency marginal electricity scenarios are considered.

Keywords Process integration · Hydrogen · Refinery · Energy systems · Simulation · Gasification

List of symbols

$e_{\text{CO}_2,i}$	Specific CO ₂ emissions of fuel <i>i</i> (kg/GJ _{fuel})
$\dot{E}_{\text{feedstock}}$	Exergy in feedstock(s) (MW)
\dot{E}_{H_2}	Exergy in hydrogen output (MW)
e_{in}	Electricity input (MW)
e_{out}	Electricity output (MW)
$\dot{E}_{\text{net electricity}}$	Exergy in net electricity output (MW)
\dot{E}_{steam}	Exergy in steam output (MW)
Feedstock in	In Eq. (1), total energy in fuel input(s), on HHV basis (MW)
H ₂	In Eq. (1), energy in hydrogen output, on HHV basis (MW)
HHV	Higher heating value (MJ/kg)
HP steam	High Pressure steam. In Eq. (1), energy in steam output (MW)
HT shift	High temperature water–gas shift reaction
LT shift	Low temperature water–gas shift reaction
$\dot{m}_{i,\text{avoided}}$	Mass flow of fuel avoided (kg/s)
η_{el}	Efficiency of marginal electricity producer
η_{ex}	Exergy efficiency
η_{tot}	First principle total efficiency
PSA	Pressure swing adsorption
SMR	Steam-methane reforming
ΔCO_2	Fossil CO ₂ emission balance (kt/y)
ΔT	Temperature difference for heat exchange used in pinch analysis (°C)

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Introduction

Biofuel production in dedicated bio-refineries has achieved major technical improvements in the recent years. Bio-ethanol and biodiesel can be used in combustion engines alone or in various blends with traditional fossil fuels. Although technical challenges of first generation biofuel production and utilization seem to be overcome, traditional fossil fuels obtained from crude oil refining are still cheaper and more widely available. However, if more stringent environmental targets are to be met, biomass utilization is likely to increase for production of electricity, fuels or chemicals. A possible way to avoid direct competition between fossil fuels and biofuels is to incorporate renewable feedstock in crude oil upgrading stages. A benefit of this approach is that an original infrastructure can be used where a large variety of fuels and/or intermediate products can be obtained from biomass in a context with high know-how and often state-of-the-art technologies. This has also the advantage that large amounts of excess heat available in oil refineries can be used for upgrading of high-moisture biomass. For these reasons, implementing biomass-based processes in existing large petro-chemical or refining industries can potentially offer cheaper and more efficient solutions in the short-medium term (Brehmer et al. 2009; Agrawal and Singh 2009).

As a consequence of increasing sulfur content of crude oil supplies, steady increase in diesel demand and harsher environmental specifications for fuels, hydrogen, and energy demands are rising in European refineries (CONCAWE 2012). To overcome hydrogen deficits, many refineries invest in dedicated hydrogen production units (HPU) usually based on steam reforming of light hydrocarbons, e.g., natural gas. These trends lead inevitably to increased carbon dioxide (CO₂) emissions from the refinery (Reinaud 2005) since both demands are covered by additional fossil fuel. However, alternative hydrogen production routes exist such as water electrolysis and thermal dissociation or biomass conversion. From a sustainability point of view, electrolysis may prove an interesting pathway if renewable-based electricity is used. Thermal dissociation of water by means of nuclear energy is a source of environmental concerns. The use of solar energy is a promising possibility but thermal dissociation itself has low hydrogen yields. Finally, biomass-based processes are promising sustainable routes. Among others, gasification offers high efficiency especially if combined with appropriate heat recovery measures, which could help reduce both dependence on fossil feedstock and emissions of fossil CO₂ (Dincer and Zamfirescu 2012).

The substitution of an existing, fossil fuel-based HPU in a large European refinery with a process based on indirect steam gasification of woody biomass (indicated in the

following by the acronym BioH₂) is investigated in this study. The focus is put on opportunities for heat integration and polygeneration.

Previous work

Although no large scale demonstration plants have been built so far, a large body of literature has been produced on stand-alone hydrogen production through biomass gasification. Spath et al. (2005) published detailed design parameters and economic results for a process based on the Batelle Columbus Laboratory gasifier. Williams et al. (2007) provide a literature review on existing gasifier concepts with focus on technological challenges. More recently Kalinci et al. (2012) conducted a study on hydrogen production processes based on biomass gasification by applying exergoeconomic analysis. Tock and Maréchal (2012) used a multi-objective optimization framework to design and optimize the thermo-economic performance of biomass-to-hydrogen concepts. The integration of stand-alone hydrogen production with other industrial plants was also investigated in a number of publications. Andersson and Harvey (2007) compared hydrogen production via pulp mill-integrated black liquor gasification and stand-alone biomass gasification. Concerning hydrogen for refining purposes, Sarkar and Kumar (2010) studied production via biomass gasification for upgrading of bitumen from oil sands. They considered stand-alone processes producing hydrogen sent via pipeline to the refining site. Johansson et al. (2012) investigated CO₂ emission consequences of hydrogen production through biomass gasification compared to standard methane reforming in a simple oil refinery equipped only with atmospheric distillation, naphtha reformer, and necessary treatment. Several process designs were included and opportunities for use of refinery excess heat were studied. In this latter study, gradual substitution of fossil-based hydrogen with biomass derived one was, however, not investigated and the biomass gasification process was considered as a supplementary capacity installed to satisfy an increase in hydrogen demand.

Objectives

In this paper, the substitution of a refinery HPU with a process based on biomass gasification is studied. Not only total substitution is considered, but also partial substitution where the two processes are operated simultaneously in the refinery. The energy and CO₂ consequences of gradual substitution of the current HPU with the BioH₂ process are shown. Few significant system configurations are then put

forward, both at partial or total substitution. Different degrees of integration with the refinery and different polygeneration concepts are considered in these system configurations. All concepts are evaluated and compared with the help of performance indicators and fossil CO₂ balances.

Methodology

Heat and power integration

To estimate theoretical energy and CO₂ balances of the proposed configurations, a targeting methodology was used whereby maximum heat recovery opportunities are considered.

The synthetic routes for hydrogen production are based on several process steps requiring heating and cooling at various temperature intervals. A set of relevant thermal streams belonging to the current HPU was extracted from actual process data. A set of relevant streams of the BioH₂ process was obtained by means of energy and mass balance calculations through simulation in ASPEN Plus (Aspen-Tech 2010).

Maximum heat recovery between system heat sources and sinks was estimated by means of Pinch Analysis tools, which were first developed by Linnhoff and coworkers in the late 1970s. Thorough descriptions of the Pinch methodology can be found in numerous publications; Smith (2005) and Klemes et al. (2010) are among the most recent. The so-called Grand Composite Curve (GCC) is used to represent aggregated heat demand and availability versus temperature level of the process. Depending on the polygeneration concept, the possible integration of an additional heat recovery steam cycle was studied graphically by plotting its GCC against that of the remaining system streams. Accordingly, the maximum steam cycle net power generation is found when at least one pinch point is activated between the process and the steam cycle, which allows exploiting the maximum heat integration potential (Marechal and Kalitventzeff 1996). Individual temperature differences were used when applying Pinch Analysis tools to better account for stream characteristics, their values are clarified in a further section of this paper.

Performance indicators

To compare the performances of the different system configurations, different indicators were used. Each indicator is based on different assumptions on the energy quality of the system products and raw materials. Using multiple indicators helps in highlighting unique features of the polygeneration concepts. First principle total efficiency η_{tot} is calculated on HHV basis according to Eq. 1:

$$\eta_{\text{tot}} = \frac{H_2 + e_{\text{out}} + \text{HP steam}}{\text{Feedstock}_{\text{in}} + e_{\text{in}}} \quad (1)$$

The main reason why no agreement is taken in the scientific community on which single indicator is most appropriate is that a first principle energy efficiency, commonly considered in energy system analysis, may be misleading when dealing with polygeneration systems as it assumes that all products (hydrogen, HP steam, and electricity in this study) and all process demands (fuels, electricity) are equivalent in terms of energy quality. A better comparison of polygeneration systems can be done by means of the exergy efficiency where different energy commodities participate only with their work generation potential, i.e., steam has much lower exergy content than electricity (Bejan et al. 1996). To this end, exergy efficiencies η_{ex} were calculated in this work for the different polygeneration concepts, according to Eq. 2.

$$\eta_{\text{ex}} = \frac{\dot{E}_{H_2} + \dot{E}_{\text{net electricity}} + \dot{E}_{\text{steam}}}{\dot{E}_{\text{feedstock}}} \quad (2)$$

A general agreement on the use of exergy efficiency for any kind of industrial plant has, however, not been reached since work production potential is not necessarily the most appropriate measure of a product intrinsic quality (e.g., for materials production). Nevertheless, exergy efficiency fits this study since all products are used in the production of automotive fuels, which will ultimately be used to produce shaft work.

Fossil CO₂ balance

To compare the environmental performances of the selected systems against the current HPU, the fossil CO₂ emissions balance (ΔCO_2) was calculated as in Eq. 3 with the assumptions shown in Table 1. In all calculations, biomass is assumed to be 100 % CO₂-neutral. CO₂ emissions associated with the use of butane and fuel gas in the current HPU were calculated under the assumption that every carbon atom in the feed ultimately produces a molecule of CO₂. CO₂ emissions associated with electricity production or demand are also taken into account by estimating the effect on marginal electricity production. Two marginal electricity producers were considered for this purpose: Natural gas combined cycle (NGCC) and coal power plants (CPP). When HP steam is produced and exported to the refinery, it is assumed that fuel gas is saved in the refinery boilers.

$$\Delta\text{CO}_2 = e_{\text{CO}_2, \text{el}} \times \frac{\text{Net electricity}}{\eta_{\text{el}}} - e_{\text{CO}_2, \text{C}_4} \times \dot{m}_{\text{C}_4 \text{ avoided}} - e_{\text{CO}_2, \text{fg}} \times \dot{m}_{\text{fuel gas avoided}} \quad (3)$$

System models

The refinery studied in this work is located on the West coast of Sweden. The plant has a capacity of 11.4 Mt crude oil/y (220,000 bpd). Hydrogen demand in the refinery is high and the amount produced through catalytic reforming does not cover the whole demand: 7.4 t/h need to be produced in a dedicated HPU. Fuel gas-fired boilers in the refinery produce 49.6 MW of High pressure steam (HP steam at 390 °C and 39 bar) with an efficiency of 80 %. A large amount of excess heat is also available from the refinery, mostly in process streams currently cooled by air fans.

To discuss the energy and environmental consequences of gradual substitution of the HPU with the BioH₂ process we refer to “H₂ Island” as the system based on the current HPU and the BioH₂ process in different proportions. Since the current HPU also exports 25 t/h of HP steam to the refinery (see following paragraph), the analysis was conducted with the condition that no deficit is created in the system. This means that in all cases, the H₂ Island provides the refinery with the same amount of hydrogen and at least the same amount of HP steam. Any potential additional steam generation and export is referred to later as “export steam”. To clarify the system boundaries considered in our study, a general representation of the H₂ Island is given in Fig. 1.

HPU

The HPU relies on a commercial, well-established technology. Steam reforming of desulfurized hydrocarbons is followed by shift reaction and hydrogen purification via pressure swing adsorption (PSA) (see Fig. 2). The unit can accommodate naphtha and butane as feedstock, both pure or as mixtures of varying proportions. For CO₂ and energy balances, a pure butane feed is assumed in this work. Data from the refinery show that with a yield of 0.3 t of H₂/t of

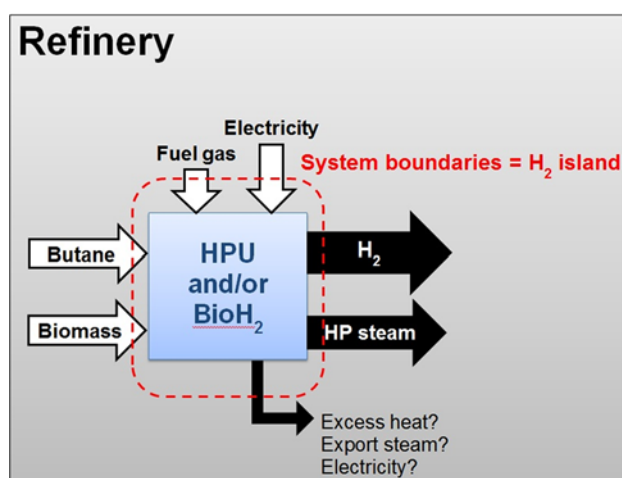


Fig. 1 System boundaries and main outputs and outputs

butane, a butane feed of 24.3 t/h is needed to produce 7.4 t/h of hydrogen. Thanks to process internal heat recovery, the HPU is energy self-sufficient and around 25 t/h of HP steam (15.9 MW) are produced and exported to other refinery units. The HPU electricity demand amounts to 2 MW (personal communication with refinery staff).

The GCC of the current HPU is given in Fig. 3. Heating of the pre-reformer and reformer feed and heat required for the reforming reaction were not included in the process streams. For technical reasons, heat at this temperature level is provided via fuel gas firing in a furnace and heat exchange with other streams is not a viable solution. Therefore, these streams were not included among the process heat sinks. For consistency issues, this implies that energy released in the furnace to heat these streams was not included as heat source in the curve either. The GCC shows no hot utility demand, which means that apart from the 29.4 MW of fuel gas fired in the reforming furnace not included in the figure, all energy demand in the process is covered by internal heat recovery. To insure that the 25 t/h of HP steam would be produced in all cases, a stream for steam generation was included in the HPU stream set. As a result, the GCC seems balanced and excess heat from the HPU is available below 240 °C only.

BioH₂ process

Unlike steam reforming of fossil feedstock, hydrogen production through biomass gasification is still at research stage, the main technological issues being related to gasification and gas cleaning as the produced gas contains a non-negligible amount of tars (heavier, condensable hydrocarbons) that need to be removed prior to further processing.

Table 1 Parameters used in CO₂ balances

Marginal electricity producer		
	Efficiency η_{el}	Specific emissions $e_{CO_2,el}$ (kg CO ₂ /GJ _{fuel})
NGCC	0.55	57
Coal power plant	0.43	92
Fuel-specific emissions e_{CO_2} (kg CO ₂ /GJ _{fuel})		
Fuel gas $e_{CO_2,fg}$	53	
Butane $e_{CO_2,C4}$	61.2	

Data on marginal electricity producers from Gode et al. (2011)

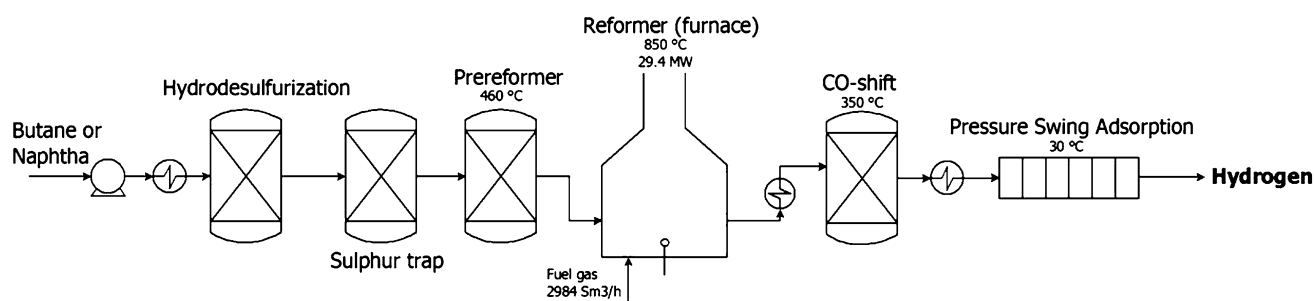


Fig. 2 Process flow diagram for refinery existing hydrogen production unit

In this work the BioH₂ process starts with air drying and atmospheric, indirect steam gasification of forest residues which composition is given in Table 2. Indirect gasification allows producing nitrogen-free syngas, a clear advantage compared to direct air-blown gasifiers when compression is required in downstream units. The need for pure oxygen production, which would put both a cost and energy penalty on the process, is also avoided. This is made possible by the indirect heat transfer between char combustion and biomass gasification areas through a circulating bed material. As shown in Fig. 4, gasification is followed by cold gas cleaning consisting of a cyclone, a cooler and a filter for particulate cleaning and a water scrubber for tar and alkali removal. The syngas upgrading section consists in steam reforming (SMR), dual shift, and PSA for hydrogen purification. Heat is provided to the reforming reactor by burning part of the syngas and 20 % of the PSA off gas. The remaining part of PSA off gas is recycled to the PSA feed stream. Part of the produced hydrogen is also recycled to the PSA feed stream in order to obtain a hydrogen concentration of 70 % at the PSA input. Heat recovery from flue gases is assumed to occur above 150 °C. Hydrogen is produced at 99.9 % purity and compressed to 27 bars in order to be fed to the refinery hydrogen distribution system.

The BioH₂ process was simulated in ASPEN Plus (AspenTech 2010). Air drying prior to the gasifier was

modelled according to (Holmberg and Ahtila 2005). The indirect gasifier was modelled considering thermodynamic equilibrium of H₂, CO, CO₂ and H₂O, and correlation factors for methane and tars yields. Methane content at the output of the gasifier was set at 10.1 % (vol%, dry gas) at the operating temperature of 850 °C (Hofbauer and Rauch 2000). Total tars yield was set at 3.5 g/Nm³. Tars were divided into secondary and tertiary species and temperature-dependent correlations were used to calculate the fraction of each species according to the classification and data published by Milne et al. (1998). All nitrogen and sulphur in the biomass feed are assumed to be converted to NH₃ and H₂S, respectively. Results of the gasifier simulation were validated against relevant published experimental data, notably from the FICFB gasifier in Güssing, Austria (He et al. 2012). The remaining parts of the process, from syngas cooling to PSA purification, were modelled using data from Hamelinck and Faaij (2002). Key parameters used in the simulation are given in Table 3.

As a result of process simulation, a hydrogen yield of 0.1 t of H₂/t of dry biomass was obtained for the BioH₂

Table 2 Feedstock characteristics

Proximate analysis (wt% dry basis)	
Fixed carbon	20.6
Volatile matter	76.8
Ash	2.6
Ultimate analysis (wt% dry basis)	
C	51.3
H	6.1
N	0.5
Cl	0
S	0.05
O	39.5
Ash	2.6
Moisture content, wet biomass (wt%)	50
Moisture content, after drying (wt%)	10.4
Higher heating value HHV (MJ/kg)	20.96

Composition from Hannula and Kurkela (2012), HHV calculated according to Channiwala and Parikh (2002)

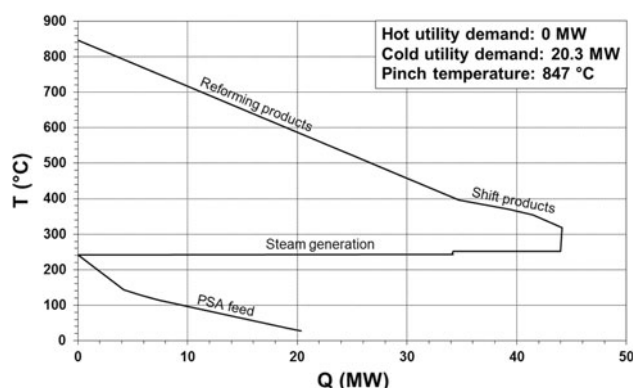


Fig. 3 GCC of the refinery hydrogen production unit

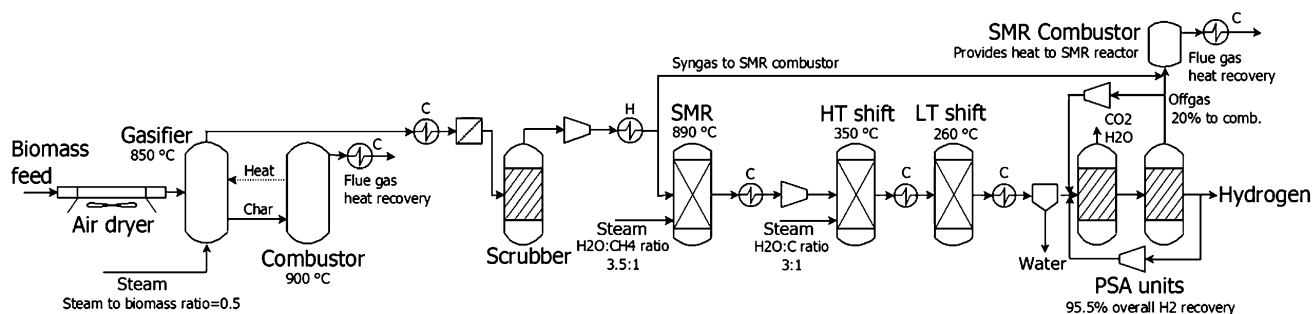


Fig. 4 Flowsheet of the biomass-to-H₂ process, as simulated in ASPEN Plus

process. This corresponds to a hydrogen-only efficiency of 67 % (MW H₂/MW biomass, HHV basis). The total process steam demand amounts to 11.6 t of steam/t of H₂. Stream data built from ASPEN Plus simulation of the BioH₂ process and used in pinch analysis is summarized in Table 4. The composition of key process streams is given in Table 5.

Hydrogen is the major component in PSA off gas, which motivates the recycle of this stream back to the PSA input in order to maximize the process hydrogen yield. To avoid buildup of impurities such as CO and CH₄, part of the offgas must, however, be taken out of the process. Burning this part to provide heat to the SMR reactor seems a relevant choice, especially given the stream composition.

The GCC for the BioH₂ process is unpinched, as shown in Fig. 5. The BioH₂ process is self-sufficient in terms of heat and steam. Biomass is used both as feedstock for hydrogen production and fuel for heat and steam generation. We observe therefore that there is no need for external fuel supply. Figure 5 also shows an excess of heat of 12.2 MW, potentially at much higher temperatures than in the refinery HPU.

Table 3 Key parameters in the BioH₂ simulation

Scrubber temperature	60	°C
SMR		
Temperature	890	°C
Pressure	15	bar
Steam to methane ratio	3.5:1	
Dual shift		
HT shift temperature	350	°C
LT shift temperature	260	°C
Pressure	22	bar
Steam to carbon ratio	3:1	
PSA		
Temperature	70	°C
Pressure, hydrogen product	20	bar
Pressure, offgas	1.3	bar
Overall H ₂ recovery	95.5	%

Selected configurations

Figure 6 presents energy and CO₂ consequences of substituting the HPU with the BioH₂ process under the assumption of maximum heat recovery within the H₂ Island. It is apparent that CO₂ emissions decrease linearly with increasing degree of substitution. The main contribution in emissions reduction is from avoided butane demand as feedstock for H₂ production.

Up to 35 % of biomass-based hydrogen production, there is enough excess heat in the HPU to cover biomass drying, which means that, up to this point, the energy available from the H₂ Island increases with the size of the BioH₂ process. At 35 % substitution, excess heat from the HPU and energy demand for drying exactly match, yielding a maximum of excess heat that can be exported from the H₂ Island. When the share of biomass-based hydrogen is further raised, an increasing amount of energy is used within the BioH₂ process for biomass drying while excess heat from the HPU decreases. This in turn reduces excess heat available from the H₂ Island.

Some possible configurations of the H₂ Island are discussed in the following and compared in terms of steam export, electricity generation potentials, and reduction of CO₂ emissions. Figure 5 shows large exergy losses in the BioH₂ process, due to the large temperature differences between process heat sinks and sources. From a pinch analysis point of view, the BioH₂ process falls into the set of so-called threshold problems since no pinch point is present and a net excess of heat appears. In fact, this excess of heat (12.2 MW) is quite small compared to the large heat pocket appearing between the hot gas cooling and the low temperature biomass drying. This means that the integration of a heat recovery steam cycle would be constrained by the drying duty and not by a pinch point with the hot gases.

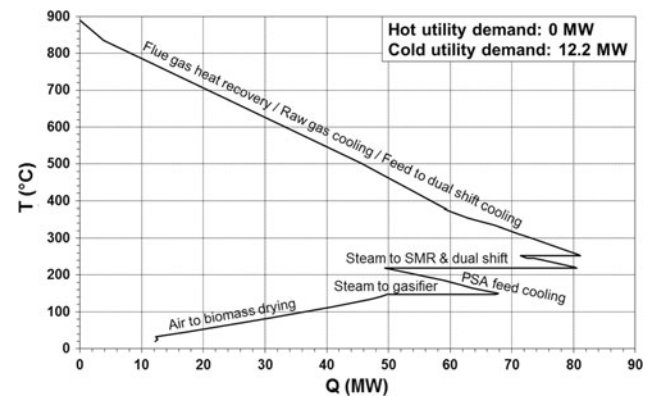
However, as mentioned earlier, a large amount of excess heat is available from the refinery. As shown in Fig. 7, even if all hydrogen demand is satisfied via the BioH₂ process, enough excess heat from the refinery is available

Table 4 Stream table of the BioH₂ process, as used in pinch analysis

Stream name	Type	T_{start} (°C)	T_{target} (°C)	Q (MW)	ΔT (°C)
Biomass drying					
D-air heating	Cold	22.5	140	52.2	10
Gasifier + gas cleaning					
G-raw gas cooling	Hot	850	130	42.2	15
G-flue gas	Hot	900	150	38.2	10
G-air preheating	Cold	15	300	12.4	10
G-water heating	Cold	15	144.2	4.7	5
G-water evaporation	Cold	144.2	144.3	17.5	2.5
G-steam superheating	Cold	144.3	500	5.7	2.5
SMR					
SMR-feed heating	Cold	295.4	860	41.1	15
SMR-water heating	Cold	16.4	216.8	6.5	5
SMR-water evaporation	Cold	216.8	216.9	15.2	2.5
SMR-steam superheating	Cold	216.9	296.7	1.5	2.5
SMR-int. compressor cooling 1	Hot	179.7	100	3.9	15
SMR-int. compressor cooling 2	Hot	232.2	150	4.0	15
SMR-air preheating	Cold	15	300	3.0	10
SMR-flue gas	Hot	900	150	17.5	10
Dual shift					
DS-HT feed cooling	Hot	890	350	35.4	15
DS-LT feed cooling	Hot	366.3	260	8.5	15
DS-LT shift	Hot	260	259.9	1.1	15
DS-water heating	Cold	16.4	216.9	7.8	5
DS-water evaporation	Cold	216.9	217	15.9	2.5
DS-steam superheating	Cold	217	230.5	0.2	2.5
DS-interstage compressor cooling	Hot	388.7	200	11.6	15
PSA					
PSA-feed cooling	Hot	260	40	46.5	15
PSA-recycle comp. int. Cooling 1	Hot	158.1	60	1.0	15
PSA-recycle comp. int. Cooling 2	Hot	187.2	100	0.9	15
PSA-product comp. int. cooling	Hot	93.7	60	1.0	15
Export steam					
Export steam—BFW preheating	Cold	109	249.5	4.1	5
Export steam—Evaporation	Cold	249.5	249.6	9.8	2.5
Export steam—Superheating	Cold	249.6	350	2.0	2.5

Table 5 Key stream compositions in the BioH₂ process from simulations (vol%, dry gas)

Component	Gasifier output	Clean gas	SMR output	Dual Shift output	PSA off gas
H ₂	40.4	41.3	58	66.1	58
CO	30.6	31.4	25.3	0.9	18.4
CO ₂	16.5	16.9	15	31.8	0
CH ₄	10.1	10.4	1.7	1.2	23.6
NH ₃	0.56	0	0	0	0
H ₂ S	0.03	0	0	0	0
Tars	1.55	0	0	0	0

**Fig. 5** GCC of the BioH₂ process

for biomass drying. The opportunity of drying biomass by means of refinery excess heat was therefore investigated and is denoted “external drying” in the following. With external drying, high temperature heat from the BioH₂ process can be fully exploited, either by heat recovery steam generation or by a heat recovery steam cycle. To highlight the benefits of external drying with respect to the case where biomass drying is carried out within the H₂ Island (internal drying), we chose to estimate the energy and CO₂ consequences for different process concepts.

The integration of the steam cycle is highlighted in Fig. 8 where the steam cycle, shown in dashed lines, is represented as a foreground subset of thermal streams against the background set of streams belonging to the BioH₂ process.

Figure 9 presents a process flow diagram of the steam cycle with its main characteristics. Heat exchangers are represented on the diagram to show key steps in the cycle but do not represent physical heat exchangers. Heat integration of the steam cycle with the BioH₂ process was investigated with pinch analysis and energy targets were calculated; the actual design of the heat exchanger network is beyond the scope of the present work.

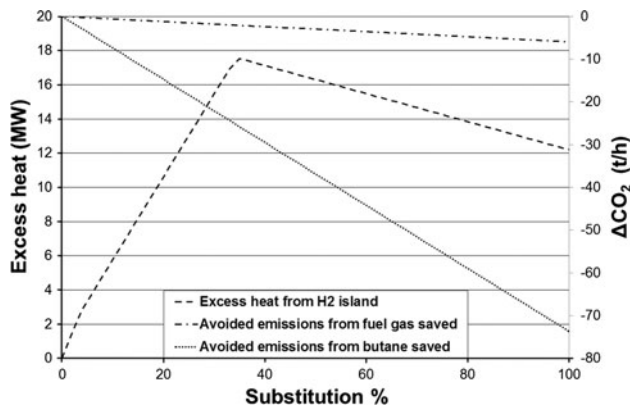


Fig. 6 Effects of gradual substitution of the HPU with the BioH₂ process

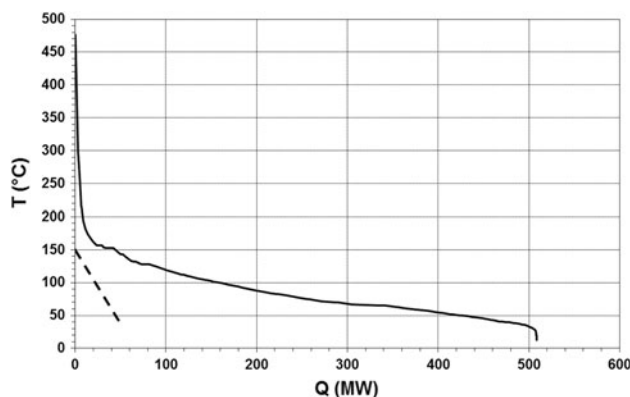


Fig. 7 Split GCC representation of external drying with refinery excess heat. *Solid line* refinery excess heat, *dashed line* energy demand for air heating in biomass drying

Four system configurations were investigated, the details of which are shown in Table 6. As was previously mentioned, 25 t/h of HP steam are exported to the refinery in all cases. Excess heat from the H₂ Island or the BioH₂ process is used alternatively to produce additional HP steam (export steam) or electricity. In Cases A and B, wet biomass (50 % moisture) enters the system whereas in Cases C and D, the input is dry biomass (10.4 % moisture, see Table 2).

Results and discussion

Energy balances

The energy balance for each case including the current HPU is presented in Table 7. For the same hydrogen production, the total energy input is higher in all configurations with the BioH₂ process than in the current HPU. This is partly due to a lower specific hydrogen yield when

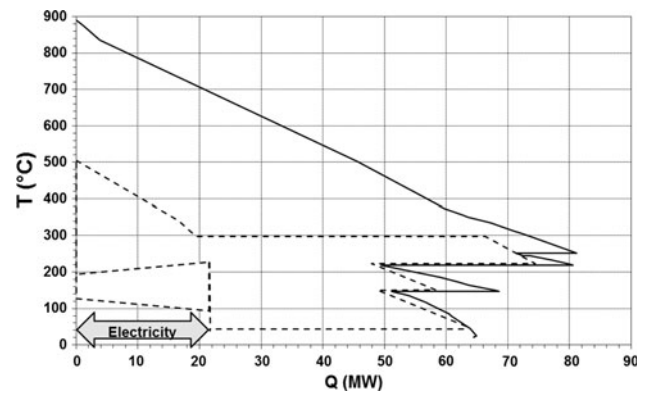


Fig. 8 Split GCC representation of steam cycle integration. *Solid line* BioH₂ process, *dashed line* steam cycle

biomass is used instead of butane. The large energy demand of biomass drying also puts a penalty on the BioH₂ process. This detrimental effect of internal drying is especially visible in Case B, where the lowest amount of products is obtained. In Case A, where biomass drying energy demand and excess heat from the remaining HPU capacity come to a perfect match, 17.5 MW of additional HP steam can be exported to the refinery, compared to only 12.2 MW in Case B.

Cases B–D all have 100 % substitution but their energy balances vary because of different ways to use excess heat from the BioH₂ process. Cases B and C both export HP steam to the refinery, but much more steam can be obtained in Case C thanks to the external drying option: an increase of export steam by 37.2 MW is observed from Case B to C. The 49.4 MW of additional HP steam export in Case C correspond to 77 t/h, which is almost equivalent to the total load of refinery boilers. Consequently, these boilers could possibly be shut down.

In Cases C and D, the same amount of heat is available from the BioH₂ process. Unlike Case C where this heat is used to export HP steam to the refinery, Case D emphasizes the opportunity of recovering such heat for electricity production through a heat recovery steam cycle. 21.8 MW of electricity can be generated in this case, which makes the BioH₂ process almost self-sufficient in terms of electricity. In all other cases, the H₂ Island is in deficit of electricity. The deficit in Cases B and C is especially large compared to the current HPU. This difference is mainly due to gas compression needed in the BioH₂ process, as opposed to the current HPU where the butane feed is compressed at liquid state.

Case D highlights the potential benefits of the opportunity for external drying. By removing the constraint of heating the air to the dryer, the integration of the steam cycle was indeed allowed until pinch points with hot gases in the BioH₂ process were activated. This in turn increased the potential for power production from a theoretical

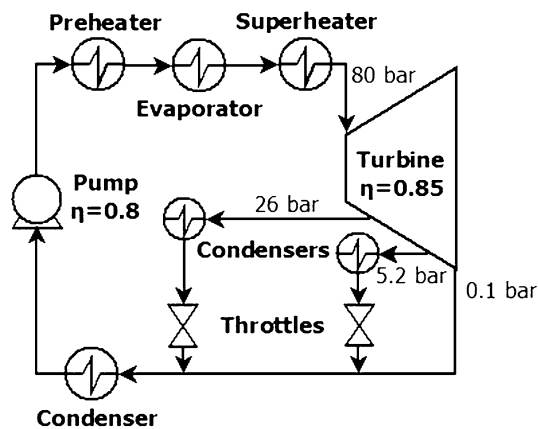


Fig. 9 Process flow diagram of the heat recovery steam cycle

Table 6 Description of investigated cases

Case	Substitution percentage	Process(es)	Biomass drying	Polygeneration products
A	35	HPU + BioH ₂	Internal	H ₂ , export steam
B	100	BioH ₂	Internal	H ₂ , export steam
C	100	BioH ₂	External	H ₂ , export steam
D	100	BioH ₂	External	H ₂ , electricity

maximum of 12.2 MW initially to 21.8 MW in Case D. Enough heat, steam, and electricity are thus produced within the BioH₂ process to satisfy all demands.

A concern about these results is about the scale of the BioH₂ system which amounts to an input of 433 MW of forest residues if all the hydrogen is produced from biomass. At present, there is no example of gasifier of this size, whether circulating fluidized bed (direct or indirect) or entrained flow. Fluidized-bed boilers are, however, commercially available at comparable scale, which suggests that future generations of gasifier could reach such sizes. Although biomass is a feedstock quite different from crude oil, the installation of two or three gasification units could overcome this scale issue and improve process controllability and flexibility.

Process performances

Table 8 shows the values of the energy and exergy efficiencies for all four cases investigated. A hydrogen only exergy efficiency of 56 % was calculated for the BioH₂ plant (i.e., only hydrogen is included as product in Eq. 2).

The highest energy efficiency (81 %) is obtained when 35 % of the hydrogen demand is satisfied by the BioH₂

process (Case A). This is in line with the energy balances presented above. The electricity deficit and the high energy demand of biomass drying in the BioH₂ process yield the lowest energy efficiency in Case B (70 %).

Performing biomass drying with refinery excess heat and producing HP steam with the high temperature heat released within the BioH₂ process allows an increase in energy efficiency by 8 percentage points between Cases B and C. Replacing steam production by electricity generation via a heat recovery steam cycle allows the BioH₂ process to be energy self-sufficient in Case D. However, this configuration yields a lower energy efficiency than the previous one, where all electricity was imported but HP steam was exported (Case C).

As was expected from the GCC and the large temperature differences between process heat sources and sinks, Case B has the lowest exergy efficiency because of large exergy losses. Cases C and D both have higher η_{ex} than Case B, which highlights the interest of process integration in the reduction of these exergy losses.

Polygeneration of steam and/or electricity yields incremental increases in η_{ex} for Cases B, C and D, which all have higher η_{ex} than the hydrogen only exergy efficiency. When biomass drying is performed with energy from within the BioH₂ process (Case B), the potential for internal heat recovery is strongly constrained and the difference between η_{ex} and the hydrogen only exergy efficiency is only 1 % point. Taking advantage of the heat pocket released by external drying and producing HP steam yields an increase of the exergy efficiency by 5 % points in Case C. Alternatively, taking advantage of this heat pocket for electricity production by means of a heat recovery steam cycle (Case D) yields the highest difference between η_{ex} and the hydrogen only exergy efficiency with 10 % points.

It is worth noting that at total substitution, i.e., among Cases B–D, the best configuration is different according to each indicator. Producing HP steam yields the highest energy efficiency with 78 % in Case C, while producing electricity—even for internal consumption—clearly appears better according to exergy efficiency (Case D). Although the load of export steam in Case C (49.4 MW) is more than twice the electricity generated in Case D (21.8 MW), steam has a much lower quality (i.e., work production potential) than electricity. A heat recovery steam cycle thus seems the best way to take advantage of the large temperature differences appearing in the heat pocket of the BioH₂ process which otherwise lead to high exergy losses as highlighted earlier. Exergy efficiency results might also give a good indication on process profitability, since electricity is generally more expensive than steam. Potentially higher revenues from electricity can, however, be made only after larger investments in steam cycle equipment.

Table 7 Energy balance

Case	Biomass feed (MW)	Butane feed (MW)	Fuel gas feed (MW)	H ₂ from HPU (MW)	H ₂ from BioH ₂ (MW)	Export steam (MW)	Electricity balance (production–demand = net) (MW)
HPU	0	334.1	29.4	291.5	0	0	0–2 = –2
A	152	217.3	20.3	189	102.5	17.5	0–9 = –9
B	433	0	0	0	291.5	12.2	0–22 = –22
C	433	0	0	0	291.5	49.4	0–22 = –22
D	433	0	0	0	291.5	0	21.8–22 = –0.2

15.9 MW of HP steam, not shown in the table, are also produced in all cases to match the production of the current HPU

Table 8 Performance indicators, results

Case	η_{tot} (%)	η_{ex} (%)
A	81	67
B	70	57
C	78	61
D	72	66

Set aside the fossil versus renewable feedstock discussion, it appears from the efficiencies obtained that the HPU performs better than the BioH₂ process. It must be stressed again, however, that the raw material for the HPU is butane, which is obtained in the refinery through several energy-intensive steps as part of crude oil refining. In that sense, the polygeneration concepts studied in this work represent the last step in feedstock transformation into hydrogen. To assess the viability of the biomass-to-hydrogen route compared to the fossil-based route would require cradle-to-gate efficiency calculations.

Fossil CO₂ balance

Table 9 summarizes the fossil CO₂ balance for each case studied. These numbers can be compared to the total CO₂ emissions in the refinery, which amounted to 1670 kt in 2010.

Because of the electricity deficit in the BioH₂ process, additional power has to be imported from the grid. Therefore, high CO₂ emissions from the marginal electricity producer yields lower reduction potentials. This can be observed in Table 9 where potentials for CO₂ emission reduction are, without exception, lower when coal power plants are the marginal electricity producers.

With NGCC as marginal electricity producer, the greatest potential for emission reduction is found in Case C, whereas it is found in Case D if electricity is imported from coal power plants. These results mean that boilers in the studied refinery emit slightly more CO₂ than a 22 MW NGCC power plant but much less than a corresponding coal power plant. This is especially valuable when deciding how to use available excess heat from the BioH₂ process: if

Table 9 Fossil CO₂ balances

Case	Fossil CO ₂ balance (kt/y) depending on marginal electricity producer	
	NGCC	CPP
A	–200	–165
B	–538	–462
C	–592	–516
D	–586	–579

CO₂ emission mitigation alone is considered, the decision will largely depend on marginal electricity production technology. If scenarios with cleaner electricity generation are considered for the future, it appears from these results that importing electricity from the grid to the BioH₂ process and exporting steam (Case C), thereby avoiding fuel gas consumption in refinery boilers, would be the most promising configuration in terms of reduction of fossil CO₂ emissions.

In all presented calculations, biomass was considered 100 % CO₂-neutral. This implies that all CO₂ released during combustion is counted as CO₂ absorbed by the plant during its growth. It can be argued that this assumption is not sound, especially if life cycle analysis is applied (Johnson 2009). However, trying to account for biomass CO₂ emissions is very difficult. An attempt to take harvesting and transportation emissions into account was, however, made here by using a value published by Gode et al. (2011), corresponding to 97 % neutrality for forest residues collected and transported inside Sweden. With this new assumption, the greatest change was found to be a 5 % increase in ΔCO_2 , i.e., the potential for emission reduction decreased by 5 %. Values were still negative for all cases, which means that they still yielded potential reductions of fossil CO₂ emissions. It would also be valuable to include not only CO₂ but all greenhouse gas emissions associated with the use of biomass, since studies have shown that nitrogen oxides emissions are especially high compared to fossil fuel-based processes. Such calculations are, however, beyond the scope of this work. Examples of emission evaluations including other greenhouse gas can be found in (Čuček et al. 2012).

Conclusions

The substitution of a fossil fuel-based refinery hydrogen production unit with a process based on biomass gasification was studied in this work. Simulation data and actual refinery data were used as inputs to pinch analysis tools to investigate energy integration opportunities. The impact of gradual substitution on energy and fossil CO₂ balances was evaluated and it was shown that avoided butane usage was the main contribution to potential emission reduction. A maximum in excess heat available from the H₂ Island was also detected at 35 % substitution. Four cases were designed from these results, both at partial and total substitution, and compared using energy and exergy efficiency. Process integration opportunities were highlighted and proved to increase both energy and exergy efficiencies of the proposed polygeneration concepts. The highest energy efficiency was obtained when steam was exported to the refinery while electricity generation through a heat recovery steam cycle yielded the highest exergy efficiency. All cases investigated yielded potential CO₂ emission reductions. The electricity deficit in the biomass-to-hydrogen process yielded lower potentials when coal power plants were considered as marginal electricity producers. If more efficient future scenarios are considered for marginal electricity production, steam export to the refinery appears the most promising option in terms of potential for reduction of CO₂ emissions.

An interesting effect of implementing the biomass-based process in the refinery is that an excess of fuel gas is created in the plant, both from offloading of the HPU furnace in all cases and from the reduced loads in refinery boilers in cases A–C. However, fuel gas is an unavoidable byproduct of crude oil refining and its utilization is an important parameter in refinery operation. In future works, it might be interesting to consider this given amount of fuel gas as a constant raw material to be used in the polygeneration concepts. Possible alternative utilizations could be, e.g., firing in a gas turbine to increase electricity production, using as a combined feedstock to the reforming reactor or using to heat the SMR reactor of the BioH₂ process instead of burning part of the syngas.

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